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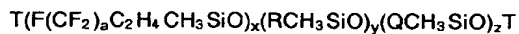
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(54) **Fluorosilicone polymer and curable fluorosilicone polymer composition.**

(57) A fluorosilicone polymer, and a curable composition having utility as a release coating which contains the polymer, are disclosed, said polymer having the structure



wherein T is a monovalent group selected from triorganosiloxy radicals or hydroxyl radicals, R is a monovalent group selected from hydrocarbon radicals or substituted hydrocarbon radicals, Q is an alkenyl radical having 4 to 8 carbon atoms, a is an integer having a value of at least 4, x, and z are integers, each having a value of at least 1, y is an interger having a value of 0 or at least 1, with the proviso that $(x + y + z) \geq 50$, $x/(x + y + z) \geq 0.25$ and $z/(x + y + z) \leq 0.1$.

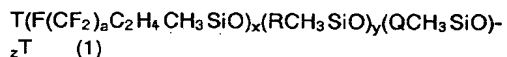
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This invention relates to a type of fluorosilicone polymer and to a curable fluorosilicone polymer composition.

In the prior art, it has been known for a long time that by forming a peelable curable coating on the surface of various substrate materials such as paper, synthetic resin film, synthetic fiber cloth, etc., it is possible to obtain a material which displays a release property with respect to pressure-sensitive adhesive or other adhesive substances. Usually, a curable organopolysiloxane composition is used as the material for forming the release coating. Examples include curable organopolysiloxane compositions made of vinyl radical-containing organopolysiloxane, organohydrodienepolysiloxane having silicon-bonded hydrogen atoms, organic compound having perfluoroalkyl radicals, and a platinum series compound (see Japanese Kokoku Patent Application No. Sho 63-48901) or curable organopolysiloxane compositions made of diorganopolysiloxane containing fluoroalkyl radicals and vinyl radicals, organohydrogenpolysiloxane, and a platinum series compound (Japanese Kokai Patent Application No. Sho 63-320). However, for these conventional types of curable organopolysiloxane compositions, the curing rate is low, and the release character is poor.

The object of this invention is to solve the aforementioned problems by providing a type of fluorosilicone polymer composition characterized by the fact that it has a high curing rate and it can form a cured coating with a low surface tension after curing. This invention also provides a type of novel fluorosilicone polymer used as the main component of the aforementioned fluorosilicone polymer composition.

This invention therefore provides a type of fluorosilicone polymer having the formula



where T represents a triorganosiloxy radical or hydroxyl radical; R represents a monovalent hydrocarbon or substituted hydrocarbon radical, Q represents a C4-8 alkenyl radical, a is an integer equal to or larger than 4, x is an integer equal to or larger than 1, y is 0 or an integer equal to or larger than 1, and z is integer equal to or larger than 1, with the proviso that $(x + y + z) \geq 50$, $x/(x + y + z) \geq 0.25$, and $z/(x + y + z) \leq 0.1$.

The present invention also relates to a type of curable fluorosilicone polymer composition comprising

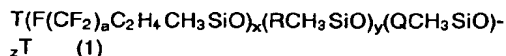
- (A) the above described fluorosilicone polymer (1);
- (B) an organohydrogenpolysiloxane which has two or more silicon-bonded hydrogen atoms on

average in each molecule, said hydrogen atoms being bonded to different silicon atoms thereof;

(C) a hydrosilylation catalyst; and

(D) an optional inhibitor for the catalyst.

According to this invention, the fluorosilicone polymer is represented by formula



where T represents a triorganosiloxy radical or hydroxyl radical. Preferably, the triorganosiloxy radical is selected from dimethylalkylsiloxy, dimethylfluoroalkylsiloxy or trialkylsiloxy radicals. Examples of the triorganosiloxy radicals that may be used include trimethylsiloxy radical, dimethylvinylsiloxy radical, 5-hexenyldimethylsiloxy radical, $F(CF_2)_aC_2H_4(CH_3)_2SiO$ radical, etc. In formula (1), R represents a monovalent hydrocarbon radical having 1 to 12 carbon atoms, such as methyl radical, ethyl radical, or other alkyl radical; phenyl radical or a substituted hydrocarbon radical, such as, trifluoropropyl radical. Preferably, R has ≤ 6 carbon atoms, methyl radical being preferred. Q represents an alkenyl radical having 4 to 8 carbons, such as hexenyl radical, heptenyl radical, butenyl radical, and pentenyl radical. Among them, hexenyl radical is preferred. The subscript "a" represents an integer equal to or larger than 4, usually 12 or smaller, such as 4, 6, or 8. The subscript "x" represents an integer equal to or larger than 1. The subscript "y" represents 0 or an integer equal to or larger than 1. The subscript "z" represents an integer equal to or larger than 1. The sum of x, y, and z, that is, $(x + y + z)$, is an integer equal to or larger than 50, $x/(x + y + z) \geq 0.25$, $z/(x + y + z)$ is 0.1 or smaller.

According to this invention, the units of $(F(CF_2)_aC_2H_4CH_3SiO)$ in the fluorosilicone polymer are the necessary structural units needed for realizing a low surface tension. The units of (QCH_2SiO) are the units needed for obtaining the curable composition. According to this invention, when a vinyl radical or allyl radical is used in place of Q in the fluorosilicone polymer, the curing rate decreases or a completely cured coating cannot be formed. That is, it has been found that the units of (QCH_2SiO) are needed for realizing a high curing rate and for realizing a completely cured state. Although the reason is not yet clear, it is believed that, because the fluoroalkyl side chains of the units of $(F(CF_2)_aC_2H_4CH_3SiO)$ are long, the short side chains such as vinyl radicals or allyl radicals, could be sterically hindered.

According to this invention, the fluorosilicone polymer is used as the main component of the following listed curable composition. That is, the curable fluorosilicone polymer composition com-

prises the following components:

(A) The fluorosilicone polymer represented by formula (1), (B) an organohydrogenpolysiloxane which has on average two or more silicon-bonded hydrogen atoms in each molecule, with these hydrogen atoms bonded to different silicon atoms, (C) a hydrosilylation catalyst, and (D) an optional inhibitor for the hydrosilylation catalyst.

According to this invention, the organohydrogenpolysiloxane (B) used in the curable fluorosilicone polymer composition is a crosslinking agent for component (A). In order to act as a crosslinking agent, it has to have two or more silicon-bonded hydrogen atoms in each molecule. Examples of the organohydrogenpolysiloxane include:

- i) $(\text{CH}_3)_3\text{SiO}((\text{CH}_3)_2\text{SiO})_p(\text{CH}_3\text{HSiO})_q\text{Si}(\text{CH}_3)_3$ - (where p and q are integers equal to or larger than 2);
- ii) $(\text{CH}_3)_3\text{SiO}(\text{F}(\text{CF}_2)_a\text{C}_2\text{H}_4\text{CH}_3\text{SiO})_r(\text{CH}_3\text{HSiO})_q\text{Si}(\text{CH}_3)_3$ (where r and q are integers equal to or larger than 2);
- iii) $(\text{CH}_3)_3\text{SiO}(\text{F}(\text{CF}_2)_a\text{C}_2\text{H}_4\text{CH}_3\text{SiO})_r(\text{CH}_3\text{HSiO})_q\text{Si}(\text{CH}_3)_3$ (where p, q and r are integers equal to or larger than 2, and a is an integer equal to or larger than 4);
- iv) $(\text{CH}_3)_2\text{HSiO}(\text{F}(\text{CF}_2)_a\text{C}_2\text{H}_4\text{CH}_3\text{SiO})_r(\text{CH}_3\text{HSiO})_q\text{SiH}(\text{CH}_3)_2$ (where r and q are integers equal to or larger than 2);
- v) $(\text{CH}_3)_2\text{HSiO}(\text{F}(\text{CF}_2)_a\text{C}_2\text{H}_4\text{CH}_3\text{SiO})_r((\text{CH}_3)_2\text{SiO})_p(\text{CH}_3\text{HSiO})_q\text{SiH}(\text{CH}_3)_2$ (where p, q and r are integers equal to or larger than 2, and a is an integer equal to or larger than 4);
- vi) $(\text{CH}_3)_2\text{HSiO}(\text{F}(\text{CF}_2)_a\text{C}_2\text{H}_4\text{CH}_3\text{SiO})_r((\text{CH}_3)_2\text{SiO})_q\text{SiH}(\text{CH}_3)_2$ (where r and q are integers equal to or larger than 2); and
- vii) copolymers made of methyl-(perfluorobutylethyl)siloxane units, dimethylhydrogen siloxane units, and SiO_2 units etc. In particular, in order to have a good compatibility with component (A), the above types (ii), (iii), (iv), and (v) are preferred.

The amount of this component should be appropriate to ensure that the ratio of the molar amount of the silicon-bonded hydrogen atoms in this component to the sum of the molar amount of the alkenyl radicals in the composition is in the range of (0.5:1)-(20:1), preferably in the range of (0.5:1-3:1). Usually, for 100 parts by weight of component (A), its amount is in the range of 0.3-40 parts by weight. This is because if the amount of component (B) is too small, the cure rate is too low. On the other hand, if the amount of component (B) is too large, the peeling property of the cured coating tends to decrease.

According to this invention, the catalyst for the hydrosilylation reaction used as component (C) is a

catalyst for crosslinking and curing components (A) and (B). Examples include micron-size platinum particles adsorbed on a carbon powder carrier, chloroplatinic acid, alcohol-modified chloroplatinic acid, olefin complex of chloroplatinic acid, coordination compounds of chloroplatinic acid and divinylsiloxane, platinum black, palladium, rhodium catalyst, etc. The amount of the component is appropriate for a catalyst. Usually, for 1 million parts by weight of component (A), the amount of the catalyst should be in the range of 0.1-100 parts by weight.

According to this invention, the optional inhibitor for the hydrosilylation catalyst used as component (D) acts to suppress the catalytic activity of the hydrosilylation catalyst at room temperature, and it is used to improve the storage stability of this composition at room temperature. Examples of component (D) include 3-methyl-1-butyn-3-ol, 3,5-dimethyl-1-hexyn-3-ol, 3-methyl-1-pentyn-3-ol, phenylbutynol, and other alkynyl alcohols; 3-methyl-3-pentene-1-yne, 3,5-dimethyl-1-hexene-3-yne, (tetramethylvinylsiloxane) cyclic compound, bis(2-methoxyisopropyl) maleate, and benzotriazole.

If needed, the composition may also be diluted with an organic solvent. Examples of the organic solvents that may be used include tetrahydrofuran and other ethers; methyl isobutyl ketone and other ketones; trifluorotoluene, hexafluoroxyethylene, and other aromatic hydrocarbons; trichloroethylene, perchloroethylene, 1,1,1-trichloroethane, dichloroethane, 1,1,2-trichlorotrifluoroethane, and other halogenated hydrocarbons; CHCl_2CF_3 , $\text{CH}_3\text{CCl}_2\text{F}$ and other HCFC-type solvents, inter alia. It is preferred that the aforementioned organic solvents be used so as to improve the storage stability of this composition and to improve the coatability on various types of substrates.

The composition of this invention can be manufactured easily by blending said components (A)-(D) or by blending components (A)-(D) together with the organic solvent to form a uniform mixture.

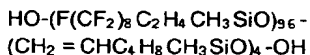
The curable fluorosilicone polymer composition of this invention can be coated on the surface of a glass plate, metal sheet, paper, synthetic resin film, cloth, or other substrates, followed by heat treatment to form a cured coating having a low surface tension. The heat treatment may be performed at a temperature in the range of 120-150 °C for a heating time of 20-30 sec. The obtained cured coating has a low surface tension, and hence it has an excellent mold release property, and the cured coating also has excellent water repellency, and oil repellency. In addition, it displays an excellent mold release property with respect to adhesives, in particular the pressure-sensitive silicone adhesives.

As explained above, the fluorosilicone polymer of this invention is useful as the feed material for forming a cured coating having a low surface tension. In addition, for the curable fluorosilicone polymer composition of this invention, because a cured coating with a low surface tension can be formed after curing, it can be used to form a cured coating with an excellent mold release property, water repellency, and oil repellency. In addition, it can be used as a mold release agent for silicone pressure-sensitive adhesive.

In the following, this invention will be explained in more detail with reference to the examples. In these examples, Vi represents vinyl radical.

Example 1

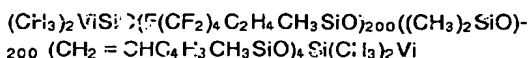
Five grams of zinc oxide, 100 g of xylene hexafluoride, and 70 g of ethyl acetate were loaded in a flask, followed by heating with reflux. Then, while being stirred, a mixture of 122 g of $F(CF_2)_8C_2H_4CH_3SiCl_2$, 1 g of $CH_2=CHC_4H_8CH_3SiCl_2$, and 45 g of xylene hexafluoride were added dropwise. After addition was completed, heating with reflux was continued for 2 hours, followed by cooling. Then 100 g of water and 45 g of hydrochloric acid were added. The separated organic layer was further washed with water till it was neutral, followed by removal of ethyl acetate, thus forming an oil-like substance. The oil-like substance was analyzed by means of gel permeation chromatography (GPC) using monodisperse polydimethylsiloxane as a standard, and it was found that the weight average molecular weight (Mw) of the polymer formed was 6,700. Then 400 ppm of trifluoromethane sulfonic acid were added to the polymer for polymerization at 50 °C for 10 hours, forming a polymer with an Mw of 50,000. From the results of the GPC analysis and nuclear magnetic resonance (NMR) analysis, it was found that the polymer had the structure:



Example 2

Four hundred grams of water were loaded into a flask. While the contents were stirred, a mixture of 361 g of $F(CF_2)_8C_2H_4CH_3SiCl_2$, 129 g of $(CH_3)_2SiCl_2$, 4 g of $CH_2=CHC_4H_8CH_3SiCl_2$, and 500 g of heptane was added dropwise. After the end of this addition, stirring was continued for 2 hours, and then it was allowed to sit. The separated organic layer was further washed with water to neutralize it. Then a water trap was installed to remove the water by heating at reflux. The heptane was removed under a reduced pressure to provide

an oil-like substance. Then 3.9 g of a compound represented by $(CH_3)_2ViSiO(F(CF_2)_8C_2H_4CH_3SiO)_{10}Si(CH_3)_2Vi$ and KOH in an amount appropriate to ensure a Si/K ratio of 5000 were added, followed by polymerization at 110 °C for 10 h. Carbon dioxide gas was blown into the aforementioned reaction system for neutralization, followed by removal of the volatile components under a vacuum to result in an oil-like polymer. From the analytical results, it was found that the polymer had the structure:



Example 3

Twenty grams of the polymer obtained in Example 1, 1 g of the compound represented by formula $(CH_3)_2HSiO(F(CF_2)_8C_2H_4CH_3SiO)_3((CH_3)_2SiO)_3(CH_3)_2HSiO)_3Si(CH_3)_2H$ and 40 g of 1,1,2-trichlorotrifluoroethane were blended uniformly. Then 0.01 g of bis(2-methoxyisopropyl) maleate and a complex of chloroplatinic acid and divinyltetramethylsiloxane with an amount corresponding to 50 ppm of metallic platinum were added and blended. This composition was coated on a glass plate, followed by heat treatment at 150 °C for 30 sec, forming a fully cured coating. The contact angle of the cured coating was measured using the liquid droplet method with the aid of a contact angle meter manufactured by Kyowa Surface Chemistry Co., Ltd. Each round of measurement was performed for 10 liquid droplets, and the mean value was then used as the contact angle. It was found that the contact angle for water was 121°, the contact angle for methylene iodide was 105°, and the contact angle for n-hexadecane was 71°.

Example 4

Ten grams of the polymer obtained in Example 2, 1 g of the compound represented by formula $(CH_3)_2HSiO(F(CF_2)_8C_2H_4CH_3SiO)_3((CH_3)_2SiO)_3Si(CH_3)_2H$ and 40 g of 1,1,2-trichlorotrifluoroethane were blended uniformly. Then 0.01 g of bis(2-methoxyisopropyl) maleate and a complex of chloroplatinic acid and divinyltetramethylsiloxane with an amount corresponding to 50 ppm of metallic platinum were added and blended. This composition was coated on a glass plate, followed by heat treatment at 150 °C for 30 sec, forming a fully cured coating. Then the contact angle of the cured coating was measured. It was found that the contact angle for water was 110°, and the contact angle for methylene iodide was 80°.

Comparative Example 1

An oil-like polymer represented by the formula $\text{HO}-(\text{F}(\text{CF}_2)_8\text{C}_2\text{H}_4\text{CH}_3\text{SiO})_{100}(\text{CH}_2=\text{CHCH}_3\text{SiO})_4-\text{OH}$, as in Example 1, was prepared in the same way except that 0.71 g of $\text{CH}_2=\text{CHCH}_3\text{SiCl}_2$ was used in place of 1 g of $\text{CH}_2=\text{CHC}_4\text{H}_8\text{CH}_3\text{SiCl}_2$.

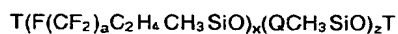
Twenty grams of the polymer obtained above, 1 g of the compound represented by formula $(\text{CH}_3)_2\text{HSiO}(\text{F}(\text{CF}_2)_8\text{C}_2\text{H}_4\text{CH}_3\text{SiO})_3((\text{CH}_3)_2\text{SiQ})_3-(\text{CH}_3\text{HSiO})_3\text{Si}(\text{CH}_3)_2\text{H}$ and 40 g of 1,1,2-trichlorotrifluoroethane were blended uniformly. Then 0.01 g of bis(2-methoxyisopropyl) maleate and a complex of chloroplatinic acid and divinyltetramethylsiloxane with an amount corresponding to 50 ppm of metallic platinum were added and blended to form a curable organopolysiloxane composition. This composition was coated on a glass plate, followed by heat treatment at 150°C for 30 sec. However, a fully cured coating was not formed.

Comparative Example 2

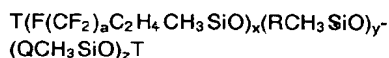
An oil-like polymer was prepared in the same way as in Example 2 except that 1.42 g of $\text{CH}_2=\text{CHCH}_3\text{SiCl}_2$ was used in place of 2 g of $\text{CH}_2=\text{CHC}_4\text{H}_8\text{CH}_3\text{SiCl}_2$. Ten grams of the polymer obtained above, 1 g of the compound represented by formula $(\text{CH}_3)_2\text{HSiO}(\text{F}(\text{CF}_2)_8\text{C}_2\text{H}_4\text{CH}_3\text{SiO})_3-(\text{CH}_3)_2\text{SiO})_3\text{Si}(\text{CH}_3)_2\text{H}$ and 40 g of 1,1,2-trichlorotrifluoroethane were blended uniformly. Then 0.01 g of bis(2-methoxyisopropyl) maleate and a complex of chloroplatinic acid and divinyltetramethylsiloxane with an amount corresponding to 50 ppm of metallic platinum were added and blended to form a curable organopolysiloxane composition. This composition was coated on a glass plate, followed by heat treatment at 150°C for 30 sec. However, a fully cured coating was not formed.

Claims

1. A fluorosilicone polymer selected from polymers having the formula



and

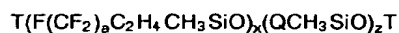


wherein T is a monovalent group selected from triorganosiloxy radicals and hydroxyl radicals, R is a monovalent group selected from hydrocarbon radicals and substituted hydrocar-

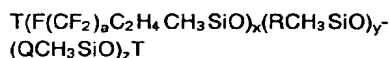
bon radicals, Q is an alkenyl radical having 4 to 8 carbon atoms, a is an integer having a value of at least 4, x, y and z are integers, each having a value of at least 1, with the proviso that $(x + y + z) \geq 50$, $x/(x + y + z) \geq 0.25$ and $z/(x + y + z) \leq 0.1$.

2. The fluorosilicone polymer of claim 1, wherein R is selected from the group consisting of methyl, ethyl, phenyl and trifluoropropyl radicals.
3. The fluorosilicone polymer of claim 2, wherein T is selected from the group consisting of trimethylsiloxy, dimethylvinylsiloxy, 5-hexenyl-dimethylsiloxy and hydroxyl radicals.
4. The fluorosilicone polymer of claim 3, wherein a is 4 to 12, inclusive.
5. The fluorosilicone polymer of claim 4, wherein R is a methyl radical.
6. The fluorosilicone polymer of claim 5, wherein Q is a hexenyl radical.
7. A curable fluorosilicone polymer composition comprising:

(A) A fluorosilicone polymer selected from polymers having the formula



and



wherein T is a monovalent group selected from triorganosiloxy radicals and hydroxyl radicals, R is a monovalent group selected from hydrocarbon radicals and substituted hydrocarbon radicals, Q is an alkenyl radical having 4 to 8 carbon atoms, a is an integer having a value of at least 4, x, y and z are integers, each having a value of at least 1, with the proviso that $(x + y + z) \geq 50$, $x/(x + y + z) \geq 0.25$ and $z/(x + y + z) \leq 0.1$;
(B) an organohydrogenpolysiloxane having on average at least two silicon-bonded hydrogen atoms in each molecule, said hydrogen atoms being bonded to different silicon atoms and the amount of said organohydrogenpolysiloxane being such that the molar ratio of said silicon-bonded hydrogen to total alkenyl groups in said composition is 0.5:1 to 20:1;

(C) a curing amount of a hydrosilylation catalyst; and
(D) optionally an inhibitor for said catalyst.

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EUROPEAN SEARCH REPORT

Application Number

EP 93 10 6739

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
X	EP-A-0 378 420 (DOW CORNING CORPORATION) * claim 4 * * page 2, line 46 - line 51 * * page 3, line 23 - line 40 * * page 5, line 5 - line 10 * -----	1-7	C08G77/24 C08L83/08 C09D183/08
D,X	EP-A-0 251 483 (DOW CORNING CORPORATION) * claims 1,2,9,10 * * page 3, line 46 - page 4, line 9 * * page 5, line 7 - line 9 * * page 6, line 33 - line 46 * * page 7, line 1 - line 11 * -----	1-7	
P,A	EP-A-0 535 597 (DOW CORNING TORAY SILICONE COMPANY, LIMITED) * claims * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			C08G C08L C09D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 JULY 1993	Examiner KANETAKIS I.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	